Executive Summary

Having successfully progressed through its planning, design and implementation stages, the Photochemical Assessment Monitoring Stations (PAMS) program is currently undergoing a shift in emphasis to focus more acutely on the analysis and interpretation of the data generated. Such a change in direction is necessary to fully realize the value of this rich and voluminous data set in a regulatory and policy context.

The PAMS networks produce a wealth of information invaluable to the development and evaluation of ozone control strategies and programs. In addition to providing a long-term perspective on changes in atmospheric concentrations of ozone and its precursors, the PAMS program will specifically help to improve emissions inventories, assist in evaluating the performance of photochemical grid models, furnish information to evaluate population exposure, and provide routine measurements of selected hazardous air pollutants. Data from PAMS will also allow for the development of the critical feed-back mechanism to evaluate the efficiency and effectiveness of emission control programs. Most importantly, PAMS will assist in deriving a more complete understanding of tropospheric ozone formation and transport, so that we may move toward the best solution to this complex environmental problem.

This document presents example analyses illustrating the utility of PAMS data across the range of ozone management applications. Where appropriate, limited critical evaluation is also included to suggest future program refinements. The document is organized in a functional manner based on mix of methodology and objectives. The Chapters describe general data characterization approaches, methods for evaluating emissions inventories, the relationship of PAMS data to emissions and observation based modeling, and quality assurance of the PAMS data.

CHARACTERIZATION OF AMBIENT AIR QUALITY FOR OZONE AND ITS PRECURSORS

Accurate characterization of ozone and its precursors is extremely important for understanding tropospheric ozone formation and accumulation, and crafting effective control strategies to address this environmental issue. Analyses have demonstrated that PAMS data are invaluable in characterizing ozone episodes and identifying features that may be linked to significant pollutant transport. For example, evidence of potentially significant pollutant transport

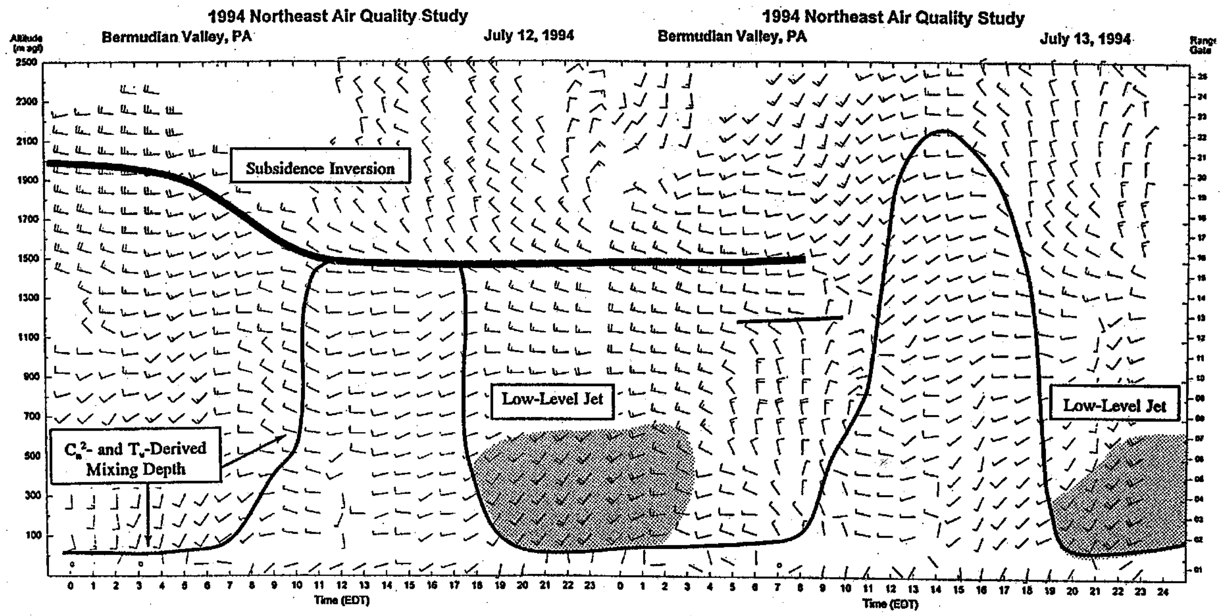


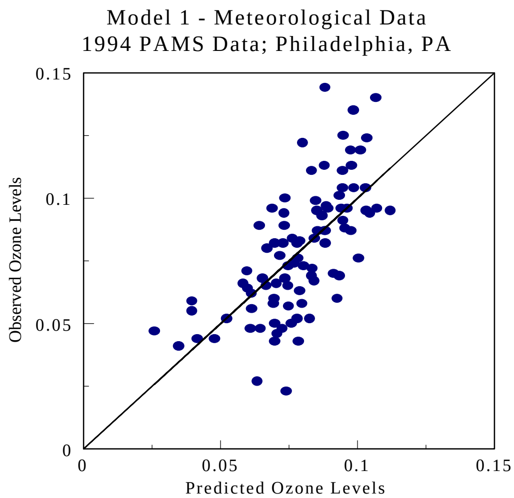
Figure E-1. Time series cross-section of winds, mixing depth, and inversion conditions measured on July 12-13, 1994 at Bermudian Valley , PA, indicating jet formation and mixing depths. The thin solid line denotes the height of the mixed layer and the thick line denotes the subsidence inversion. Each wind barb indicates direction and speed. (Lindsey et al., 1995).

(e.g, detection of a nocturnal jet as shown in Figure E-1) can be identified by combining PAMS hourly surface and upper air meteorological data. In addition, the PAMS requirement for routine measurements of organic species allows improved characterization of precursor conditions

associated with ozone episodes and provides, for the first time, a data set sufficiently detailed to power statistical investigations of the relationships between ozone and its precursors. For example, Figure E-2 compares observed ozone levels from Philadelphia, PA in 1994 with predicted ozone levels produced by two statistical models. The first uses only meteorological data to predict ozone levels while the second adds hydrocarbon data as an input. The improvement in the model's ability to "explain" downwind ozone (when hydrocarbon data are included) clearly demonstrates the value of speciated volatile organic compound (VOC) data in accurately characterizing and understanding ozone concentrations. A more detailed description of how PAMS data can be used to better characterize ambient conditions can be found in Chapter 1.

PAMS DATA IN SUPPORT OF OZONE MODELING APPLICATIONS

PAMS data support emissions-based model (EBM) applications by providing additional information for evaluating (1) model predicted concentrations for ozone and its precursors; and (2) meteorological and emissions inputs which drive model simulations. The use of PAMS data



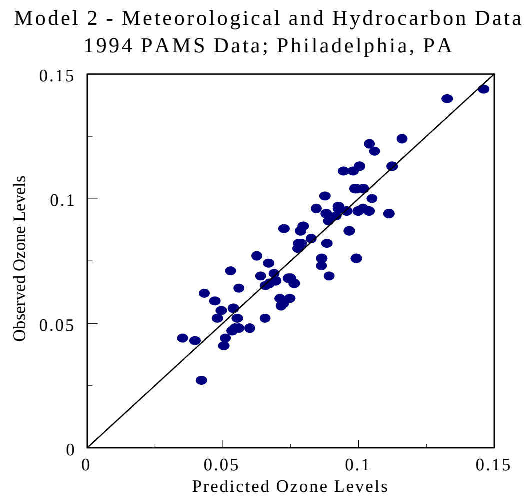


Figure E-2. Comparisons of Observed Ozone Levels with Those Predicted from Two Statistical Models Using Data from Philadelphia, PA (Model 1, R2=0.45; Model 2, R2=0.89)

to evaluate model simulated concentrations of ozone and its precursors is an important incremental contribution to the overall model performance evaluation. The addition of PAMS precursor measurements reduces the degrees of freedom in the model evaluation process and (assuming acceptable model performance) increases the probability that the model is correctly predicting surface ozone for the right reasons rather than as a result of compensating errors. In addition, the upper air meteorological monitoring requirements of PAMS yield improvements in the representativeness of simulated wind fields and mixing heights (as shown previously in Figure E-1) both of which are critically important inputs to the EBMs. Finally, key use of the PAMS speciated VOC data is the evaluation of emissions inventories (a significant component of EBMs). Such evaluations with PAMS data provide insight into the number and mix of emissions sources as well as potential gaps in emissions configurations. An example illustrating the value of PAMS-like data in model evaluation is taken from a study performed in Texas. On August 19, 1993, a highly localized ozone peak of 231 ppb was observed in Houston for which the modeling results did not replicate the timing or the magnitude. A series of across-the-board emissions sensitivity runs for VOC and oxides of nitrogen (NO_x) failed to improve model performance. An analysis of nearby VOC data indicated an anomalous peak in the total non-methane hydrocarbons (NMHC). Through further analysis of the ambient speciation, the emissions inputs were adjusted to coincide with the ambient data. Subsequent model runs resulted in improved representation of the peak ozone as shown in Figure E-3. A more detailed explanation of this example and a thorough discussion of the use of PAMS data as a means of improving EBM simulations is provided in Chapter 2.

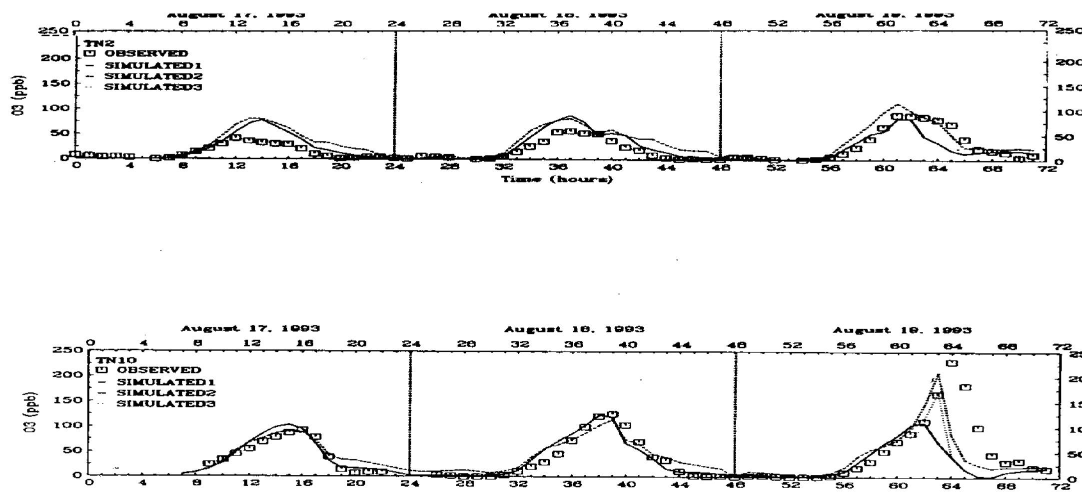


Figure E-3. Time series plots of ozone at two sites before and after correction in emissions. Notice that simulated ozone changed significantly at site TN10, responding to emissions change, and little change occurred at site TN2 (top).

EVALUATION OF EMISSIONS FACTORS, MODELS AND INVENTORIES USING PAMS DATA

As mentioned previously, data from the PAMS program provide an important tool for evaluating and refining estimates of ozone precursor emissions. The concept of using ambient measurements to improve emissions models, factors and inventories is not new, having been first used to evaluate particulate matter inventories in the 1970's. To date, several interpretive techniques have been used to evaluate emissions inventories with the PAMS data. Types of screening analyses include comparisons of ambient- and emissions-derived hydrocarbon / NO_x ratios, association of certain compounds with transport direction, time series analyses, and the detection of chemical species associated with certain events or episodes. Multi-variate models (e.g., factor analysis, Source Apportionment by Factors with Explicit Restrictions (SAFER), Chemical Mass Balance (CMB)) can also be used to interpret the data. Such analyses and studies can reveal missing sources and/or suggest improvements to the spatial or temporal resolution of the emissions inventory. They can also determine the need for better emissions factors or activity inputs to emissions models or factors.

For example, data collected during the 1991 Lake Michigan Ozone Study (LMOS) were used to compare emissions inventory and ambient concentration ratios of non-methane organic compound (NMOC), NO_x, and carbon monoxide (CO) for Chicago, Gary, and Milwaukee. Comparisons of 7-9 a.m. ratios for two ozone episodes (June 25-28 and July 16-18) showed that the ambient computed ratios were generally higher than the inventory ratios. The relative individual NMOC species compositions of the ambient and inventory data were also examined. As a result of LMOS, the Lake Michigan Air Directors Consortium (LADCO) reevaluated the emissions inventory and made several significant changes to the point, area, and mobile source figures. Speciation profiles and background assumptions were also revised. Tables E-1 and E-2 below show the computed ambient and emission $NMOC/NO_x$ ratios both before and after the LADCO inventory revision. Chapter 3 provides a more complete discussion of how PAMS data can be used to help improve emissions estimates.

Table E-1. Lake Michigan Area - Ambient Versus Original Set of Emissions Inventory $NMOC/NO_x$ Ratios, 1991 (Korc, 1993)

Site	Ambient $NMOC/NO_x$	Emissions $NMOC/NO_x$	Ambient/EI
Gary[a]	5.3	4.3	1.2
Chicago	4.8	2.6	1.9
Milwaukee[a]	6.4	4.2	1.6

[a] Ambient $NMOC/NO_x$ ratios correspond to June 26, July 16 and 18, 1991

Table E-2. Lake Michigan Area - Ambient Versus Revised Set of Emissions Inventory $NMOC/NO_x$ Ratios, 1991 (Korc, 1993)

Site	Ambient $NMOC/NO_x$[b]	Emissions $NMOC/NO_x$	Ambient/EI
Gary[a]	4.8	5.0	1.0
Chicago	4.7	3.6	1.3
Milwaukee[a]	6.4	3.8	1.7

[a] Ambient $NMOC/NO_x$ ratios correspond to June 26, July 16 and 18, 1991

[b] Ambient $NMOC/NO_x$ with background correction

OBSERVATIONAL-BASED METHODS FOR DETERMINING VOC/NO_x EFFECTIVENESS

Observational-based methods, which require ambient precursor measurements as inputs, can provide directional guidance on the relative effectiveness of reducing NO_x or VOC in reducing ozone levels. As such, they serve as an important means of corroborating results obtained from EBMs. The PAMS program provides ambient air quality data of greater spatial, temporal and compositional detail than previously available and therefore improves the basis for exercising observational methods. For example, the Georgia Institute of Technology (GIT) observational-based model (OBM) requires detailed speciated VOC measurements of the type provided by PAMS. Figure E-4 illustrates an application of the GIT-OBM for Atlanta covering several monitoring locations. The model provides a relative assessment of the role of emissions groups on ozone formation. Descriptions of the uses of PAMS data in several observation-based methods are presented in Chapter 4.

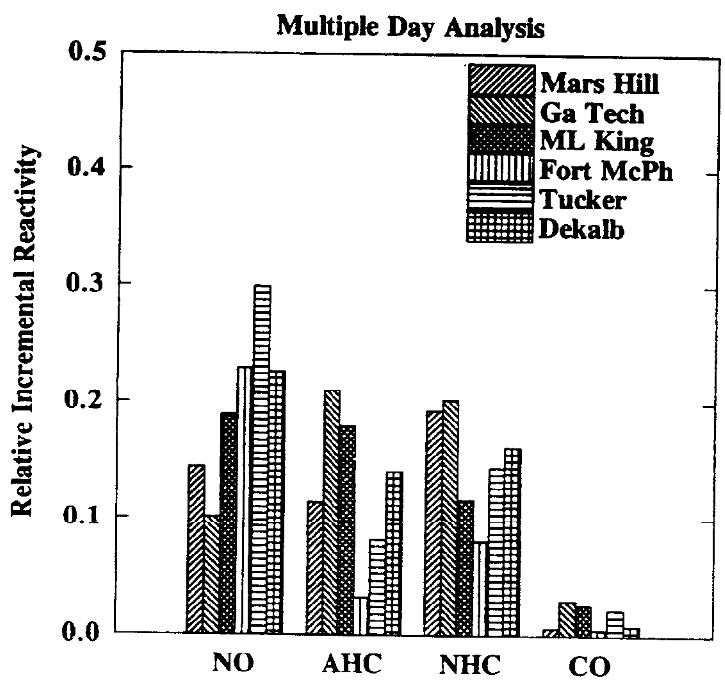


Figure E-4. Results from GIT-OBM applied to Atlanta. (Cardelino and Chamiedes, 1995).

LINKAGES AMONG TECHNIQUES

Although the examples are presented in this report as distinct entities to facilitate unambiguous descriptions, the significance of the individual analysis areas to the ozone management process is best understood when they are considered as elements of an integrated whole. For example, the value of spatial, temporal and speciated displays of ozone and precursor data is considerably greater when such displays are viewed as techniques to quality assure data and provide direction for more refined analysis. Similarly, the significance of emissions inventory evaluations is more substantial in the context of their use in improving (or corroborating) the inputs to photochemical models. The results from the application of OBMs are far more important when coupled with results from more traditional EBMs.

The step-wise air quality modeling process can be used as a framework to illustrate the linkages among these analysis categories. The modeling process can be viewed as sequential four-step process:

1. Selecting model days or episodes and specifying modeling domain;
2. Developing and evaluating meteorological and emissions inputs;
3. Testing and evaluating the model under present conditions; and
4. Applying the model in a control strategy context and evaluating/corroborating performance.

Basic data characterization efforts for air quality and meteorology form the basis for almost all model process elements. The selection of appropriate model days historically has been based on a review of meteorology and ozone data. PAMS provides these elements, and adds highly resolved upper air meteorological data and precursor data as additional factors in episode selection. Transport and aging related analyses yield other considerations in characterizing the days to be modeled. Perhaps the most important contribution of PAMS to the modeling process is an improved ability to evaluate the basic emissions and meteorological inputs to drive the simulations. The examples contained in this report describe the unique contributions of PAMS data in resolving vertical mixing phenomena (mixing heights and winds) and providing a continuous, speciated record of hydrocarbon compounds to check emissions estimates. The spatial and temporal data characterizations are also applied in evaluating “current” day EBM behavior. Finally, greater confidence in emissions-based models’ predictive abilities (i.e., the ability to correctly reflect ozone response to emissions changes) is gained when observational-based models (which independently assess control strategy preference) produce agreement. Combined with a longer term trends perspective, the PAMS data can be used to continuously check the predicted response of the model leading to iterative analyses and refinements when measurements diverge from original projections. This longer term approach speaks to the greatest value of PAMS - a long-term record for ongoing evaluations of control programs.